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(54) Title: METHOD FOR STABILIZING AN ORGANIC MATERIAL WHICH IS SUBJECT TO THERMAL AND/OR OXIDATIVE DETERIORATION AND RESULTING STABILIZED MATERIAL

(57) Abstract

Organic materials which are subject to thermal and/or oxidative deterioration, e.g., polyether polyols and polyurethane foams prepared from polyether polyols, are stabilized against such deterioration by the addition thereto of a stabilizing amount of a liquid, crystallization-resistant mixture of phenolic esters made up predominantly of phenolic monoester(s), the mixture of phenolic esters being obtained by reacting an alkyl ester of a 3,5-dialkyl-4-hydroxyphenyl alkanoic acid with a polyhydroxyl alcohol under esterification reaction conditions employing an esterification reaction catalyst.

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METHOD FOR STABILIZING AN ORGANIC MATERIAL WHICH IS SUBJECT TO THERMAL AND/OR OXIDATIVE DETERIORATION AND RESULTING STABILIZED MATERIAL

BACKGROUND OF THE INVENTION

This invention relates to methods for stabilizing organic materials which are prone to deterioration via thermal and/or oxidative mechanisms and to the resulting stabilized materials. More particularly, the invention relates to such methods and compositions which employ hindered phenols as stabilizers.

Prior art methods for the stabilization of polyether polyols and other polymeric materials with antioxidants or other stabilizers and the use of the stabilized polyols in the preparation of polyurethane foams to inhibit scorch are well known. Polyether polyols, used in the manufacture of slabstock flexible and semiflexible polyurethane foams, are typically stabilized with antioxidant packages consisting of phenolic and amine antioxidants which may also contain synergists such as phenothiazine or various compounds containing phosphite moieties.

U.S. Patent Nos. 3,567,664 and 3,637,865 disclose the use of a mixture of 2,6-di-tert-butyl-4-methyl phenol, also referred to as butylated hydroxytoluene, or BHT, and p,p'-dialkyldiphenylamines to stabilize polyurethane foams. While BHT has been widely used for many years as a stabilizer for polymers, it is subject to several drawbacks including its relatively high volatility, its ability to sublime and its ability to form highly colored chromophores which can cause discoloration in polymers, polymer foams and materials in contact with

the polymers. Accordingly, many investigations have been undertaken to modify the chemistry of BHT to eliminate or mitigate the aforementioned drawbacks or to replace BHT entirely with some other stabilizer of equivalent or superior effectiveness.

Oxidative stabilizers similar in structure and utility to the functionalized esters derived from (4-hydroxy-3,5-dialkylphenyl)alkanoic acids are disclosed in U.S. Patent Nos. 3,644,482, 3,779,945 and 4,032,562. In U.S. Patent No. 3,644,482, the alkanoic acid esters are terminated with aliphatic hydrocarbons which is not the case in the compounds of the reaction product mixtures of the instant invention. The compounds of U.S. Patent No. 3,644,482 are isolated and crystallized which may be contrasted with the liquid mixtures of the present invention.

U.S. Patent No. 3,779,945 discloses stabilizer compositions containing mixtures of 3-(3,5-dialkyl-4-hydroxyphenyl)propionic acid esters of at least two non-identical alkanediols.

U.S. Patent No. 4,032,562 discloses phenolic stabilizers, indicated for use in polymers such as polyurethanes, which are obtained by reacting a 3,5-dialkyl-4-hydroxyphenylalkanoic acid, acid chloride or lower alkyl ester with a saturated aliphatic glycol under known esterification conditions employing as catalyst a strong acid such as para-toluene sulfonic acid. In all of the working examples, the reaction product (which would necessarily have contained a complex mixture of esterification products) was subjected to distillation to yield what appears to have been a single relatively pure

product or narrow fraction of closely related products. However, being relatively pure or being made up of closely related compounds, the distilled reaction products of U.S. Patent No. 4,032,562 are prone to crystallizing into a solid mass which is difficult to manage, especially where addition of the product to a liquid polymer such as a polyalkylene glycol or to a liquid reaction mixture providing a solid polymer, e.g., a reaction mixture providing a rigid or semirigid polyurethane slabstock, is concerned. There is no suggestion in U.S. Patent No. 4,032,562 of stabilizing a liquid polymer with the entire, i.e., the undistilled or unfractionated product, of the foregoing esterification reaction.

SUMMARY OF THE INVENTION

In accordance with the present invention, a method for stabilizing an organic material that is subject to thermal and/or oxidative deterioration is provided which comprises incorporating into such material a stabilizing amount of a liquid, crystallization-resistant mixture of phenolic esters made up predominantly of phenolic monoester(s), the mixture of phenolic esters being obtained by reacting an alkyl ester of a 3,5-dialkyl-4-hydroxyphenyl alkanoic acid with a polyhydroxyl alcohol under esterification reaction conditions employing an esterification reaction catalyst.

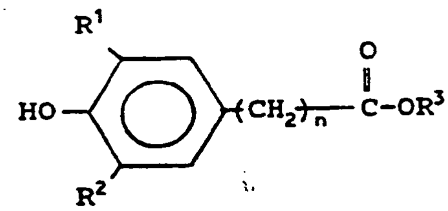
The liquid, crystallization-resistant stabilization composition employed in the method of the present invention possesses a decided advantage over stabilizers such as the distilled esterification products disclosed in U.S. Patent No. 4,032,562 that may be

initially liquid but which tend to crystallize during subsequent handling, transit or storage. Thus, the stabilization composition herein is more apt to remain liquid when its use is desired. In the case of a stabilizer composition that has solidified due to crystallization, heating is required to return the composition to the liquid state before it can be added to the organic material requiring stabilization, an inconvenience at best and a technically troublesome requirement at worst.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The stabilizer composition of this invention is obtained by reacting at least one alkyl ester of a 3,5-dialkyl-4-hydroxyphenyl alkanoic acid with at least one polyhydroxyl alcohol under esterification reaction conditions employing an esterification catalyst. The resulting reaction product comprises a complex mixture of functionalized esters of the 3,5-dialkyl-4-hydroxyphenyl alkanoic acid which are not distilled, fractionated or separated from each other to any appreciable extent prior to being added to the organic material requiring stabilization. Laboratory and chromatographic analyses reveal that the mixture of esters contains hydroxy and C_2-C_{12} alkoxy functionalized 3-(3',5'-di-t-butyl-4'-hydroxyphenyl)alkanoic acid esters of the polyhydroxyl alcohol.

The starting alkyl esters of 3,5-dialkyl-4-hydroxyphenyl alkanoic acid are preferably selected from among those of the general formula



wherein R^1, R^2 and R^3 each is the same or different and represents an alkyl group of from 1 to 6 carbon atoms and n is 0, 1 or 2. Preferred starting phenolic esters include those in which R^1 and/or R^2 are relatively bulky groups such as t-amyl, t-butyl, etc. The compounds methyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, ethyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate and propyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate are especially preferred.

The starting polyhydroxyl alcohols are preferably selected from among the aliphatic polyhydroxyl alcohols of the general formula $R(OH)_n$ wherein R is an aliphatic group of from 2 to about 12 carbon atoms and n is 2 to 7. Representative of the preferred group of aliphatic polyhydroxyl alcohols are such compounds as ethylene glycol, the propanediols, the butanediols, the pentanediols, the hexanediols, the heptanediols, the octanediols, glycerol, trimethylol propane, pentaerythritol, etc., and combinations of any of the foregoing. In the case of ethylene glycol, it may be advantageous to include another polyhydroxyl alcohol reactant so as to obtain a reaction product having greater crystallization resistance than that obtainable employing ethylene glycol alone. Diols possessing a secondary

hydroxyl group such as 1,2-propanediol and 1,3-butanediol and triols such as glycerol are especially preferred for use herein. Such alcohols tend to provide mixtures of phenolic esters having greater resistance to crystallization.

While the mole ratio of polyhydroxyl alcohol to phenolic ester reactant can be less than, equal to or greater than 1, it is generally desirable to use a molar excess of the alcohol as this is likely to increase the amount of phenolic monoester(s) in the reaction product. In general, the mole ratio of polyhydroxyl alcohol to phenolic ester can vary from about 1.2:1 to about 10:1, preferably from about 1.5:1 to about 6:1 and more preferably from about 1.7:1 to about 4:1. Suitable reaction temperatures can range from about 100° to about 190°C and preferably from about 120° to about 175°C.

Other reaction conditions that may affect the outcome of the reaction and the nature of the product mixture include the type of esterification catalyst used. Although both basic and acidic esterification catalysts can be used, it is generally preferred to employ an acidic catalyst such as p-toluene sulfonic acid, especially when the polyhydroxyl alcohol reactant contains a secondary hydroxyl group, so as to provide reaction mixtures of the greatest complexity, in turn providing mixtures of phenolic esters having the greatest crystallization resistance. Whatever the esterification catalyst used, it can generally be employed at from about 0.1 to about 10, and preferably from about 0.5 to about 2.0, mole percent of the starting phenolic ester. The reaction time will ordinarily be on the order of from about 4-5 hours.

Monitored by gas chromatographic methods, the reaction can be allowed to continue until the remaining phenolic ester reactant possesses an area percent of less than about 5%, preferably less than about 2% and more preferably less than about 1%.

The mixed phenolic ester stabilizer composition herein can be made up entirely of the product phenolic esters but can also contain substantial quantities of one or more other stabilizers, e.g., other phenolic stabilizers, amine-containing stabilizers, thioester stabilizers, phosphite stabilizers, etc.

Amine-containing stabilizers that can be used herein include the complex mixture of substituted diphenylamines containing a significant proportion of butylated and oxylated species which is obtained by reacting isobutylene and diphenylamine. These substituted diphenylamines are commercially available under the tradenames Naugard PS-30 (Uniroyal Chemical Co.) and Irganox L-57 (Ciba-Geigy Corporation). Other substituted diphenylamine stabilizers that can be used herein include Wingstay 29 (Goodyear) and Vulkanox (Mobay). Still other amine stabilizers include the phenylenediamines and mixtures of phenolic and phenylenediamine stabilizers such as are known in the art.

Examples of thioester stabilizers that can be used herein include Cyanox 711 (American Cyanamid), Argus DMTDP (Argus Chemical Co.) and Evanstab 14 and Carstab DMTDP (Evans).

Other useful stabilizers than can be added to the mixed phenolic ester stabilizer composition of this invention include the thiophenols, dimethylacridan,

phenothiazine and phosphites such as phenyl diisodecyl phosphite, tris(nonylphenyl)phosphite and, more recently, tris(2,4-di-t-butylphenyl)phosphite which has become the industry standard for hydrolytic stability.

In carrying out the method of the invention, a stabilizing amount of the stabilizing composition is added to an organic material which is susceptible to thermal and/or oxidative degradation. In particular, synthetic organic polymeric substances such as vinyl resins formed from the polymerization of vinyl halides or from the copolymerization of vinyl halides with unsaturated polymerizable compounds can be stabilized with the mixtures of functionalized esters of this invention. Specifically, these vinyl compounds would include vinyl esters, alpha, beta-unsaturated acids, esters, aldehydes, ketones and unsaturated hydrocarbons such as butadiene or styrene.

The method of this invention is also applicable to the stabilization of poly-alpha-olefins such as polyethylene, polypropylene, polybutylene, polyisoprene, and the like and copolymers of poly-alpha-olefins, polyamides, polyesters, polycarbonates, polyacetals, polystyrene and polyethyleneoxide. Included as well are high-impact polystyrene copolymers such as those obtained by copolymerizing butadiene and styrene and those formed by copolymerizing acrylonitrile, butadiene and styrene.

Other organic materials stabilized in accordance with the present invention include aliphatic ester lubricating oils, animal and vegetable-derived oils, hydrocarbon materials such as gasoline, both natural and synthetic, diesel oil, mineral oil, fuel oil, drying oil,

cutting fluids, waxes, resins and fatty acids such as soaps.

A particularly advantageous application of the method of this invention is the stabilization of polyether polyols which are thereafter reacted with isocyanates to produce polyurethane foams. The stabilization compositions of this invention impart scorch (both physical and color) protection to the polyurethane foams which are employed in such end uses as carpet underlay, bedding, furniture, automobiles (both insulation and seats) and packaging. The occurrence of scorch is of major concern to polyurethane foam manufacturers since scorch negatively affects the appearance of the product, causes physical damage and can result in fire. Therefore, foam manufacturers require enhanced scorch protection during flexible slabstock foam production. The role of antioxidants can be critical in providing increased scorch protection in urethane foams without diminishing the other properties desired by the industry.

The stabilizer composition of this invention can be incorporated into the organic material to be stabilized by known and conventional methods. In particular, the stabilizer composition of this invention can be pumped or metered into the organic material in predetermined amounts. The specific amounts of stabilizer composition employed can vary widely depending upon the particular organic material being stabilized. In general, the addition of from about 0.1 to about 2, preferably from about 0.2 to about 1 and more preferably from about 0.4 to about 0.6 percent, of stabilizer composition by weight of the organic material to be stabilized provides generally

good results. In the case of a polyurethane foam, such amounts of stabilizer composition can be added directly to a component of the polyurethane foam-forming composition, e.g., the polyol, or to the foam-forming composition itself. The following examples are illustrative of the invention.

EXAMPLE 1

This example illustrates the preparation of a liquid, crystallization-resistant mixed phenolic ester stabilization composition for use in the method of the invention.

A 5-liter bottom outlet reaction kettle with a flanged glass top was equipped with an overhead stirrer, a subsurface nitrogen sparge tube, a thermocouple probe and a Graham condenser. The Graham condenser was fitted with a simple distillation head and a condenser.

The vessel was charged with methyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate (1880 g), 1,3-butanediol (3,090 ml) and p-toluene sulfonic acid monohydrate (PTSA) (12.8 g). The mole ratio of 1,3-butanediol to phenolic ester reactant was about 5.4:1. The system was purged with nitrogen, agitated and warmed to 145°C. The system was held at 145°C for 5.5 hours. The reaction mass was allowed to cool to about 80°C and thereafter Lacolene (Ashland Chemical Co.) aliphatic petroleum naphtha (750 ml) was added. The solution was initially extracted with 0.12M sodium bicarbonate (800 ml) and then extracted three times with water (200 ml portions). Any remaining volatile matter was removed by rotary evaporation. The yield of light-colored, liquid product was 1,957 g. The product obtained was a complex mixture of phenolic esters having a moderate viscosity at room temperature.

EXAMPLE 2

This example illustrates another preparation of a liquid, crystallization-resistant mixed phenolic ester stabilization composition for use in the method of the invention.

A 5-liter bottom outlet reaction kettle with a flanged glass top was equipped with an overhead stirrer, a subsurface nitrogen sparge tube, a thermocouple probe and a Graham condenser.

The vessel was charged with methyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate (2917 g), 1,3-butanediol (1798 g), and p-toluene sulfonic acid monohydrate (19.7 g). The mole ratio of 1,3-butanediol to methyl ester was about 2:1. The system was purged with nitrogen, agitated, and warmed to 140°C. The system was held at 140°C for 9 hours. The reaction mass was allowed to cool to about 80°C and thereafter Lasolene (Ashland Chemical Co.) aliphatic petroleum naphtha (600 ml) was added. The solution was extracted five times with water (800 ml portions). Any remaining volatile matter was removed by rotary evaporation. The product obtained was a light-colored, complex mixture of phenolic esters having a moderate viscosity at room temperature.

COMPARATIVE EXAMPLE 1

This example illustrates the preparation of an essentially pure phenolic ester or mixture of closely related phenolic esters as described in U.S. Patent No. 4,032,562, discussed above.

A 2-liter bottom outlet reaction kettle with a flanged glass top was equipped with an overhead stirrer, a subsurface nitrogen sparge tube, a thermocouple probe, an inlet from a heated reservoir, and a Graham condenser. The Graham condenser was fitted with a simple distillation head and a condenser.

The reaction kettle was charged with 994.9 grams of 1,3-butanediol. Thereafter, 1128 grams of methyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate was charged into the reservoir and 7.15 grams of lithium amide was added to the reaction kettle. The entire system was purged with nitrogen and the methyl 3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate was heated until it melted. The temperature of the Graham condenser was adjusted to 65-70°C and the butanediol was heated to 150°C. The methyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate was added over three hours with agitation and nitrogen sparge. Heat treatment of the reaction mass was continued for an additional four hours.

The reaction mass was brought to 80°C followed by addition of 250 ml of xylenes. This was followed by the addition of glacial acetic acid (30 ml). The mixture was agitated, allowed to settle and the aqueous layer was removed. The mixture was washed with 400 ml of water, with 500 ml of 0.55 M sodium bicarbonate and twice more with 400 ml portions of water.

Water, xylene and other volatiles were removed by distillation at 60 torr at temperatures ranging from about 50 to about 130°C. The yield was 1250 grams of a dark liquid mixture of phenolic esters.

Such mixture is not suitable for use as an antioxidant or stabilization additive since its dark color would only discolor the material to which it is added. For example, were the dark liquid added to a polyether polyol which in turn were to be used in the manufacture of a polyurethane foam, the resulting foam would exhibit a decided discoloration which would be commercially unacceptable. Therefore, the usual practice, and one followed in U.S. Patent No. 4,032,562, is to distill the dark liquid to obtain a relatively clear product made up of a single pure phenolic ester or mixture of closely related (in terms of boiling point) phenolic esters. In the present example, the dark liquid mixture of phenolic esters was purified by distillation at 3 torr to a constant boiling point of 197°C.

EXAMPLES 3-7

Polyurethane foams stabilized with known stabilization compositions and with the mixed phenolic ester stabilization compositions of the present invention were prepared for comparison, specifically, for the degree of scorch protection provided by the stabilizers.

The polyurethane foam-forming reaction mixtures were prepared with a 3,000 average molecular weight Olin Poly-G 32-52 polyether polyol (Olin Corp.) minimally stabilized against degradation with 100 ppm of Naugard BHT (Uniroyal Chemical Company, Inc.) and further stabilized with 2000 ppm of Naugard PS-30 amine stabilizer (Uniroyal Chemical Company, Inc.). To 200g of Olin Poly-G 32-52 polyether polyol was added with stirring a premix containing 10g water, 0.20g Dabco-33LV amine catalyst (Air Products Co.), 2.9g L-620 silicone surfactant (Union Carbide, Inc.) and 14g Antiblaze 100 flame retardant (Albright & Wilson Americas). To this mixture were added 0.0146g of T-10 tin catalyst (Air Products and Chemicals) with stirring for 5 additional seconds. Finally, 131.2g of TDI-80, a 115 index toluene diisocyanate (Mobay Corp.) was added.

The reaction mixture was stirred at high speed for 7 additional seconds and then poured into a 10" x 10" x 5" cardboard box.

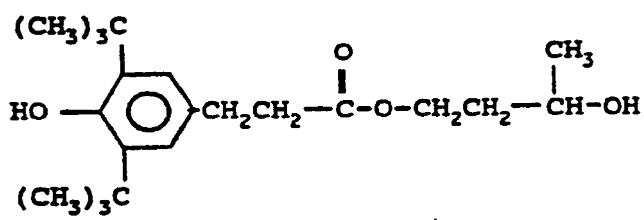
The foam was allowed to rise completely at room temperature, indicated by the appearance of bubbles across the surface of the foam bun, and then allowed to stand for 5 additional minutes. The sides of the box were removed before curing the sample for 17.5 minutes at 20% power in a GE Whirlpool microwave oven. The foams were air oven

cured for 3 minutes at 125°C immediately after the microwave cure.

Upon removal of a foam from the air circulating oven, the foam was immediately cut in half, horizontally to the rise of the foam, and analyzed for degree of scorch using the Hunterlab Colorimeter, Model D25M/L.

The performance rating of each foam is based on a scale of 1-10 with 1 being the best scorch protection and 10 being the worst.

The phenolic ester stabilizer compositions used in the foams contained various mixtures of the following compounds:



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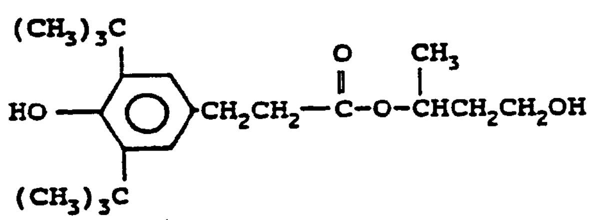

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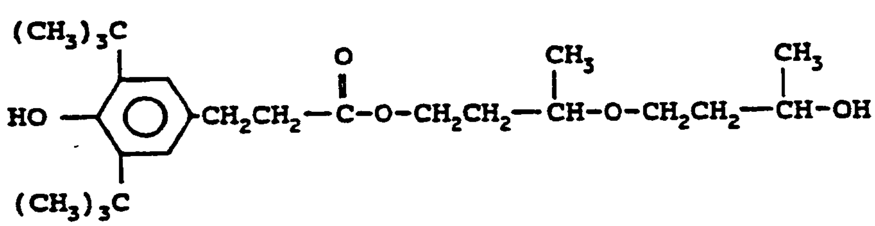

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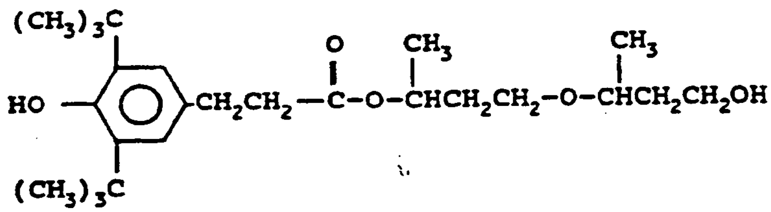

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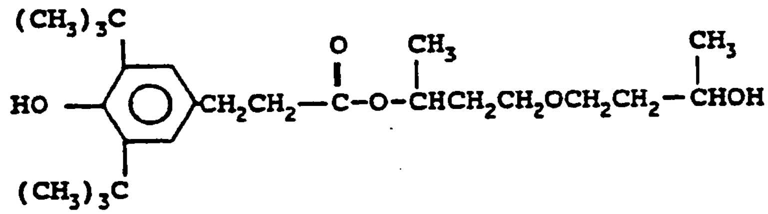

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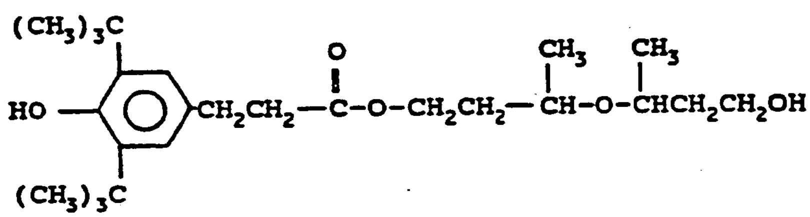

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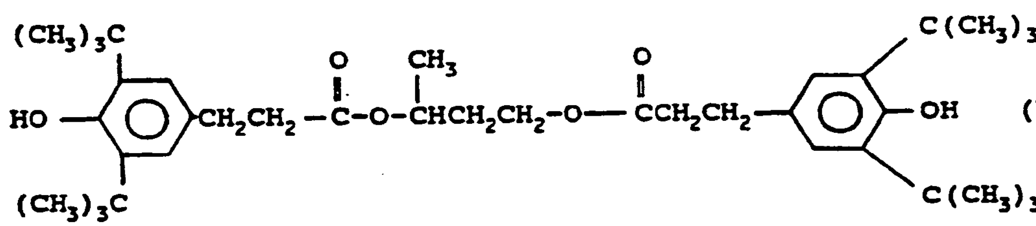


(VII)

The compositional analysis and amount of each stabilizer composition employed in each polyurethane foam-forming reaction mixture and resulting foam were as follows:

Example	Analysis of Stabilizer Compound(s)	Area %*	Amount of Added Stabilized Composition, ppm
3 (standard)	BHT		2500
4 (essentially identical to the distillate from Comp. Ex. 1)	I + II	98.6	2500
5	I + II	68	2500
	III to VI	23	
	VIII	4	
	Other compound(s)	5	
6	I + II	80	2500
	III to VI	13	
	Other compound(s)	7	
7	I + II	50	2500
	III to VI	29	
	VII	11	
	Other compound(s)	10	

*Area % by GC analysis.

The results of the scorch test for each of two separate runs were as follows:

	Scorch Rating	
Example	Run No. 1	Run No. 2
3	2+	2+
4	4	3
5	2	1-2
6	2+	2+
7	Not Run	1-2

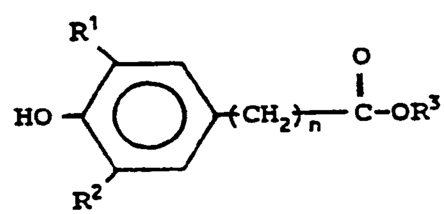
These data show that the mixed phenolic ester stabilization composition of this invention performed at least as well, and in some cases better, than the industry standard, BHT, and that the composition consistently out-performed a relatively pure phenolic ester or mixture of closely related phenolic esters (Example 3) which is illustrative of the prior art.

WHAT IS CLAIMED IS:

1. A method for stabilizing an organic material which is subject to thermal and/or oxidative deterioration which comprises incorporating into such material a stabilizing amount of a liquid, crystallization-resistant mixture of phenolic esters made up predominantly of phenolic monoester(s), the mixture of phenolic esters being obtained by reacting an alkyl ester of a 3,5-dialkyl-4-hydroxyphenyl alkanoic acid with a polyhydroxyl alcohol under esterification reaction conditions employing an esterification reaction catalyst.

2. The method of Claim 1 wherein the organic material which is subject to deterioration is selected from the group consisting of polyether polyol and polyurethane.

3. The method of Claim 1 wherein the alkyl ester of the 3,5-dialkyl-4-hydroxyphenyl alkanoic acid possesses the general formula



wherein R^1, R^2 and R^3 each is the same or different and represents an alkyl group of from 1 to 6 carbon atoms and n is 0, 1 or 2 and the polyhydroxyl alcohol possesses the general formula $R(OH)_n$ wherein R is an aliphatic group of from 2 to about 12 carbon atoms and n is from 2 to about 7.

4. The method of Claim 3 wherein the polyhydroxyl alcohol is a diol possessing a secondary hydroxyl group or a triol.

5. The method of Claim 3 wherein the esterification catalyst is an acidic esterification catalyst.

6. The method of Claim 3 wherein the mole ratio of polyhydroxyl alcohol to the alkyl ester of the 3,5-dialkyl-4-hydroxyphenyl alkanoic acid is from about 1.2:1 to about 10:1.

7. The method of Claim 3 wherein the mole ratio of polyhydroxyl alcohol to the alkyl ester of the 3,5-dialkyl-4-hydroxyphenyl alkanoic acid is from about 1.5:1 to about 6:1.

8. The method of Claim 3 wherein the polyhydroxyl alcohol is a diol possessing a secondary hydroxyl group or a triol, the esterification catalyst is an acidic esterification catalyst and the mole ratio of polyhydroxy alcohol to the alkyl ester of the 3,5-dialkyl-4-hydroxyphenyl alkanoic acid is from about 1.2:1 to about 10:1.

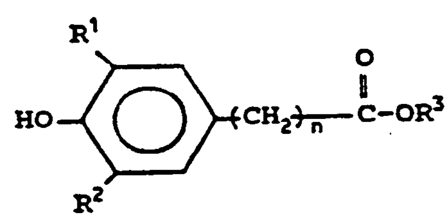
9. The method of Claim 8 wherein the aliphatic polyhydroxyl alcohol is 1,2-propanediol, 1,3-butanediol or glycerol and the alkyl ester of the 3,5-dialkyl-4-hydroxyphenyl alkanoic acid is methyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, ethyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate or propyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate.

10. The method of Claim 8 wherein the organic material which is subject to deterioration is selected from the group consisting of polyether polyol and polyurethane.

11. A composition comprising an organic material which is subject to thermal and/or oxidative deterioration and a stabilizing amount of a liquid, crystallization-resistant mixture of phenolic esters made up predominantly of phenolic monoester(s), the mixture of phenolic esters being obtained by reacting an alkyl ester of a 3,5-dialkyl-4-hydroxyphenyl alkanoic acid with a polyhydroxyl alcohol under esterification reaction conditions employing an esterification reaction catalyst.

12. The method of Claim 11 wherein the organic material which is subject to deterioration is selected from the group consisting of polyether polyol and polyurethane.

13. The method of Claim 11 wherein the alkyl ester of 3,5-dialkyl-4-hydroxyphenyl alkanoic acid possesses the general formula



wherein R^1, R^2 and R^3 each is the same or different and represents an alkyl group of from 1 to 6 carbon atoms and n is 0, 1 or 2 and the polyhydroxyl alcohol possesses the

general formula $R(OH)_n$ wherein R is an aliphatic group of from 2 to about 12 carbon atoms and n is from 2 to about 7.

14. The method of Claim 13 wherein the polyhydroxyl alcohol is a diol possessing a secondary hydroxyl group or a triol.

15. The method of Claim 13 wherein the esterification catalyst is an acidic esterification catalyst.

16. The method of Claim 13 wherein the mole ratio of polyhydroxyl alcohol to the alkylation of the 3,5-dialkyl-4-hydroxyphenyl alkanoic acid is from about 1.2:1 to about 10:1.

17. The method of Claim 13 wherein the mole ratio of polyhydroxyl alcohol to the alkyl ester of the 3,5-dialkyl-4-hydroxyphenyl alkanoic acid is from about 1.5:1 to about 6:1.

18. The method of Claim 13 wherein the aliphatic polyhydroxyl alcohol is a diol possessing a secondary hydroxyl group or a triol, the esterification catalyst is an acidic esterification catalyst and the mole ratio of polyhydroxy alcohol to the alkyl ester of the 3,5-dialkyl-4-hydroxyphenyl alkanoic acid is from about 1.2:1 to about 10:1.

19. The method of Claim 18 wherein the aliphatic polyhydroxyl alcohol is 1,2-propanediol, 1,3-butanediol or glycerol and the alkyl ester of the 3,5-dialkyl-4-hydroxyphenyl alkanoic acid is methyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, ethyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate or propyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate.

20. The method of Claim 18 wherein the organic material which is subject to deterioration is selected from the group consisting of polyether polyol and polyurethane.

INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/US 94/03037

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C08K5/13

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 032 562 (MARTIN DEXTER) 28 June 1977 cited in the application see column 1, line 13 - line 40 see examples 1-3 ---	1-20
A	EP,A,0 141 419 (B.F. GOODRICH COMPANY) 15 May 1985 see page 30, line 31 - line 32 see page 31, line 19 - line 20 see claim 1 -----	1-20

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

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Date of the actual completion of the international search	Date of mailing of the international search report
19 July 1994	-8. 08. 94

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Siemens, T

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. .nal Application No
PCT/US 94/03037

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-4032562	28-06-77	NONE		
EP-A-0141419	15-05-85	US-A-	4523032	11-06-85
		CA-A-	1325217	14-12-93
		DE-A-	3469732	14-04-88
		JP-A-	63044561	25-02-88
		JP-A-	60112737	19-06-85